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13. ABSTRACT (Maximum 200 words)

The goal of this project is to develop an understanding of kinetic-energy-enhanced effects in the processing/etching steps of semiconductor fabrication. An instrument was developed that uses a kinetic-energy-variable argon ion source together with independent dosing of neutral reactive molecules to probe the evolution of neutral and ionic products during etching. These products are probed by laser ionization. Studies determined the effects of ion beam energy on the yields of neutral and ionic silicon and silicon chloride products during the etching of silicon by chlorine. The temperature dependence of the neutral and ion products was measured.

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"Kinetic-Energy-Enhanced Neutral Etching."

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Statement of Problem Studied

The etching of silicon wafers is a ubiquitous process in semiconductor device fabrication. There have been many studies of the species formed during etching, but various aspects of the mechanisms are not completely understood. This program addressed several microscopic mechanisms of silicon etching induced by the interactions of energetic particles (e.g. argon ions) with a silicon surface under conditions of chemical dosing (e.g. molecular chlorine or fluorine). Two laser methods were developed to probe the neutral products of the etching in the presence of large fluxes of ions: laser single photon ionization at 118 nm (9th harmonic of the Nd:YAG laser) and resonantly enhanced, tunable dye laser multiphoton ionization. These techniques revealed a number of important results about the products of the etching process under realistic etching conditions.

Brief Outline of Research Findings

A new method to detect many of the neutral species produced under realistic etching conditions was developed using a method of laser flux monitoring. The method involves a pulsed vacuum ultraviolet laser source (118 nm, 9th harmonic of a Nd:YAG laser) that can ionize the neutral species during the etching process. A silicon wafer is dosed with chlorine molecules and simultaneously bombarded with an energy-variable flux of argon ions. A pulse sequence is used, so that the large fluxes of interfering ionic species are first swept from the zone in front of the wafer. Then the neutral products that were formed as a result of the ion bombardment and chemical etching process are directly interrogated with the laser and a time-of-flight mass spectrometer.

This technique of laser single photon ionization time-of-flight mass spectrometry was used to measure the neutral Si, SiCl, and $SiCl_2$ etch products during ion-enhanced etching of Si(100) for an ion kinetic energy range of 275-975 eV. The etch products were examined as a function of ion energy, ion flux, and molecular chlorine flux. Direct detection of a significant evolution of silicon neutral atoms was observed, resulting from the simultaneous action of the ion beam and the chlorine chemical reactivity. However, the SiCl product has the greatest yield by far. The yield of each product increases with increasing ion energy. However, the yield ratio of neutral SiCl/Si decreases with increasing ion energy,

suggesting a decrease in the chlorine coverage at higher ion beam energies. The results of this investigation were successfully fit to a simple kinetic model, which incorporates the chlorine coverage under realistic etching conditions and the increase in desorption of silicon with chorine coverage.

Under argon-ion-enhanced etching conditions of Si(100) by chlorine, the single photon laser ionization method was used to compare the yields of neutral etch products to the yields of ionic etch products, with the latter being measured directly by the time-of-flight mass spectrometer. There is a good correspondence between the ion and neutral products over a wide range of conditions, suggesting that most of the products are formed during the direct impact of the argon ions, rather than due to subsequent thermal chemistry and desorption after the argon ion impact. However, neutral $SiCl_2$ is observed as an etch product, whereas no yield of ionic $SiCl_2^+$ is detected at all. The latter result suggests that some neutral products may be formed by subsequent thermal reactions following the ion impact, whereas the ion products are only formed in the direct ion impact event.

The temperature dependence of the ionic and neutral yields of etch products was studied for Si(100) + chlorine with argon-ion-enhanced bombardment. The initial decrease of both the ionic and neutral products with increasing temperature suggests a decreasing chlorine coverage with temperature. However, a substantial increase in the observed ionic product yield at higher temperatures, with a secondary maximum at 800 K, suggests a very different mechanism for the formation of the ion products compared to neutral etch products. The enhanced yield of ion etch products Si^+ and $SiCl^+$ may be due to electronic properties (e.g. the availability of conduction electrons that change with temperature) in the silicon substrate when heated. The potential use of the ionic products as a means to monitor the predominant neutral etch products versus temperature is specifically ruled out.

Resonantly enhanced multiphoton ionization (REMPI) was also developed as a method to detect Si and SiCl. In addition to greater signal-to-noise achieved with the REMPI method, state-resolved detection was also successful. Initial experiments investigated the spin-orbit excited state populations of Si atoms during thermal and ion-enhanced etching. The results of such studies have the potential to reveal the

local heating by the argon ion impact, however in these studies the spin-orbit states were found to be essentially in thermal or statistical distributions, even during ion-enhanced etching.

Summary of Most Important Findings:

The most important findings are as follows: (1) measurements of the neutral and ionic product yields were obtained during thermal and ion-enhanced etching by use of single photon laser ionization time-of-flight mass spectrometry; (2) Under realistic ion-enhanced etching conditions for Si(100) by chlorine, we showed that neutral silicon atoms are released directly (in agreement with theory), but that SiCl is the most dominant product, in contrast to earlier investigations; (3) studies were performed on the temperature dependencies of the ionic and neutral products during etching; (4) resonant-enhanced multiphoton ionization was developed and used to detect the spin-orbit state distributions of atomic products during etching.

ARO Publications on Etching (1997-present):

N. Materer, R. S. Goodman, and S. R. Leone, "Laser single-photon ionization mass spectrometry measurements of SiCl and $SiCl_2$ during thermal etching of Si(100)," J. Vac. Sci. Tech. A **15**, 2134 (1997).

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N. Materer, R. S. Goodman, and S. R. Leone, "Comparison of electron cyclotron resonance and radio-frequency inductively coupled plasmas of Ar and N_2: Neutral kinetic energies and source gas cracking," J. Appl. Phys. **83**, 1917 (1998).

R. S. Goodman, N. Materer, and S. R. Leone, "Ion-enhanced etching of Si(100) with molecular chlorine: Reaction mechanisms and product yields," J. Vac. Sci. Technol. A , **17**, 3340 (1999).

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N. Materer, Rory S. Goodman, and Stephen R. Leone, "Ion-enhanced Etching of Si(100) with Molecular Chlorine: Neutral and Ionic Product Yields as a Function of Ion Kinetic Energy," J. Phys. Chem. B **104**, 3261 (2000).

T. A. Barckholtz, L. A. McDonough, and S. R. Leone, "Spin-orbit distributions of Si atoms produced during the Ar^+-enhanced etching of a Si(100) surface," in preparation.

Participants and Degrees Awarded

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Reportable Inventions:

none